

# PATENT SPECIFICATION

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## (54) RECORDING INFORMATION BY FORMING FLUORESCENT MATERIAL IMAGES

(71) We, AMERICAN CYANAMID COMPANY, a corporation organised and existing under the laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the recording and retrieval of information.

Information recording and recovery systems are of rapidly increasing importance in the present-day economy in view of the rise in the number and complexity of the data which must be recorded and be retrievable to handle the increasing every day business load, and to assist in scientific developments. Many optical systems, including those based on silver halide emulsions and the like, have contributed significantly to this development, largely because of the high packing density with good retrievable resolution inherent in such systems. Systems based on magnetic means, e.g., the well-known magnetic tape and magnetic ink check-printing systems, have likewise found great utility, largely because of the relative ease of handling and the relatively simple equipment involved, combined with, particularly in the case of tapes, high reproducible fidelity. However, the optical systems are not as versatile as desired in that only a single image is normally recorded at any one bit, e.g., the developed Ag image. The same is true of the magnetic tape images where normally only the magnetic image is obtained at any one bit. This image can be made visual by a separate step, e.g., by dusting with iron powder. The magnetic ink images have the advantage of being both visually and magnetically sensible; however, these images suffer from a relatively low packing density.

The present invention provides a new method of recording information on a substrate.

The method of this invention comprises the steps of (a) providing a substrate which carries a fluorescer precursor substance which is at least substantially non-fluorescent (as herein defined) but which is capable of being converted to a chemically different fluorescent substance on being heated or on the application of ultraviolet light, and (b) heating said substrate or applying ultraviolet light thereto, in a pattern corresponding to the information to be recorded thereon, said heating or applied ultraviolet light being such as to effect conversion of said fluorescer precursor substance to a fluorescent substance capable of fluorescing under ultraviolet or visible light whereby the information is recorded on said substrate as a pattern of fluorescent substance which corresponds to the applied information pattern.

In accordance with this invention either direct heating as by applying heated

objects or indirect heating of the precursor substance on the substrate with infrared radiation, may be employed in step (b) of the recording method.

Retrieval of information recorded on a substrate by the method of this invention may always be effected by applying to the substrate U.V. or visible light of a wavelength to cause the fluorescent substance to undergo fluorescence, and thus display the recorded image which can be detected visually or by suitable instruments. In some cases the fluorescent substance formed during the information recording step may be colored, and hence immediately visible.

It will be understood that the information formed may be of any desired type, that is alphanumeric characters, code markings such as dots or lines, or pictorial information.

In the present invention, recording of information is rapid, accurate and dry, and in preferred embodiments no fixing being required. Retrieval is rapid, exceptionally sensitive and accurate and is not accompanied by degradation. Moreover, it is possible to obtain high information density packing with the present invention.

Among the processes to which the method of the present invention has application are the electronic storage and replay of sound and pictures; numerical data collection and retrieval; and the production and validation cards, stamps, passes, or other documents.

The fluorescer precursor may be a colorless material, as may also the fluorescent substance to which it is converted. In this instance, the storage and retrieval may be unknown to all persons except those intended to have knowledge of the information storage. This could be used for placing information on passes or documents to be retained by one person and checked or authenticated by another such as in the case of a gate pass. An advantage of the present system is that any portion or entire cards or documents can be treated with the fluorescer precursor substance, even over other information or images, after which particular information may be put on the treated part by the method of this invention. It will be apparent therefore, that many cards may be produced, with individual information placed thereon at a later time, by conversion of the desired image portion to a fluorescent compound. Since the compounds are colorless in either state, space is saved in that the later information is printed over the original visible information. Detection is by means of U.V. or visible light which stimulates the fluorescent form of the material. Preferably, this stimulating radiation is of such a wavelength that it does not convert any of the remaining fluorescent precursor substance to the fluorescent substance, in order to prevent conversion of the background to the same state as the image by the detecting radiation, but where the detection is relatively of short duration, this could be done by the same wavelength radiation as used to form the image.

The present invention has a further characteristic that the amount of detectable fluorescence may be proportional to the amount of latent fluorescer which has been converted to the fluorescent state. Thus, when radiant energy is used to record the desired image, amount i.e. ultraviolet or infrared radiation, the converted on any radiated area depends on the duration of time of exposure to the irradiating energy. The longer the time period is, the more latent fluorescer there will be converted per unit of exposed area and thus the more intense the fluorescence upon subsequent radiation and detection. This characteristic makes it possible to produce detectable variable tone fluorescent radiation over a given area. This is much like the tone variation in a photographic negative or a magnetic sound tape. Thus the present invention could be used to prepare a sound tape by audio modulation of the radiant source. The sound is detectable by conventional fluorescent detection means coupled to audio output means by a suitable transducer. A sound track could be put on a movie film in the same manner, either beside the picture, or printed directly on film. A photographic disc could be prepared and played by the same principal.

Although the intensity of fluorescence increases with exposure to applied radiation, detectable radiation has been obtained with a low intensity light source at as low as one millisecond and with a laser, imaging maybe done in nanoseconds.

Examples will be given hereinafter of fluorescent precursor-fluorescent systems which are reversible i.e. the fluorescent image is erasable by the application of suitable light radiation. Other systems are not reversible in this way, but when the converted fluorescent information cannot be removed, it is possible to insert new information by blotting an old word or number by converting it entirely to a fluorescent "bar", and creating another word or number adjacent thereto in fluorescer precursor material. This, of course, is limited to the area of treatment with fluorescer precursor material.

The fluorescer precursor substance may be coated on any desired substrate, or it may be incorporated in transparent or opaque plastics films. The substrate may be

of any configuration, e.g. sheets, belts, discs, drums, and three dimensional objects such as bottles, boxes. Techniques for this will be readily apparent to persons skilled in the art. It will be obvious that choice of materials may depend on the particular intended use.

The fluorescer precursor substance may be any material which has the desired properties, that is it is a substance which is at least substantially non-fluorescent but which can be converted by means of heat or ultraviolet light to a chemically different substance which is capable of exhibiting fluorescence under U.V. or visible radiation. By the term "at least substantially non-fluorescent" is meant a substance either which exhibits no fluorescent properties at all with U.V. or visible radiation (which is preferred) or which is weakly fluorescent with U.V. or visible radiation but which is convertible by the applied information-bearing energy to a chemically different substance which fluoresces under U.V. or visible light so much more strongly than the fluorescer precursor that there will be sufficient contrast between converted and unconverted substance to enable an image pattern of the former to be read out against a background of the latter. Obviously, in any given case one chooses that form of energy which is suitable to effect the conversion of the fluorescer precursor present to the chemically different fluorescent substance.

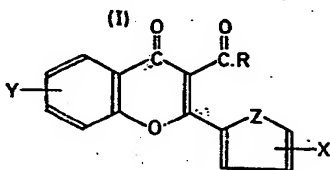
Many examples of different fluorescer precursor substances will now be given, in some cases together with details of how they may be converted to the fluorescent state. A glossary of the abbreviations (other than chemical symbols) used in the reaction equations is given below:

#### Glossary

Abbreviation	Meaning
h $\nu$	light
Fl	wavelength of maximum fluorescence intensity
$\lambda_{max}$	sensitizing dye employed
dye sens	quantum efficiency
$\phi$	fluorescence efficiency
F.E.	extinction coefficient
$\epsilon$	heat
$\Delta$	

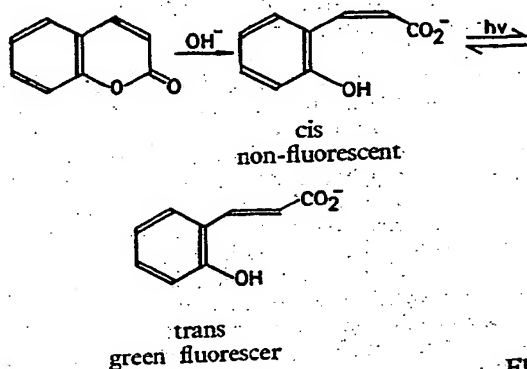
First of all, there will be described some fluorescer precursors which are convertible to a fluorescent form on being irradiated with ultraviolet light, the fluorescence being activated by light of longer wavelength than that used to effect the image formation.

(1) 2-(2-furyl or thienyl)-3-acylchromones of the formula:



in which R is phenyl, lower alkylphenyl, lower alkoxyphenyl or furyl, X is a hydrogen or lower alkyl, Y is hydrogen, lower alkyl, lower alkoxy or furyloxy and Z is oxygen or sulfur. The 2-thienyl compounds such as 2-(2-thienyl)-3-benzoylchromone, 2-(5-methyl-2-thienyl)-3-benzoylchromone and 2-(5-methyl-2-thienyl)-3-anisoylchromone are included within the scope of Formula I because their photolysis mechanism upon exposure to ultraviolet light is substantially the same as that of the 2-(2-furyl)-3-acylchromones.

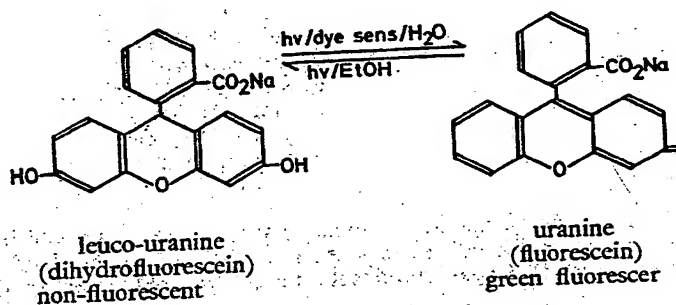
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$$\lambda_{\text{max}}^{\text{Fl}} = 510 \text{ m}\mu$$

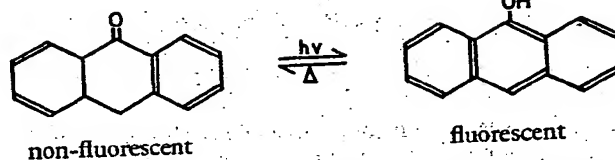
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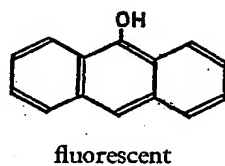
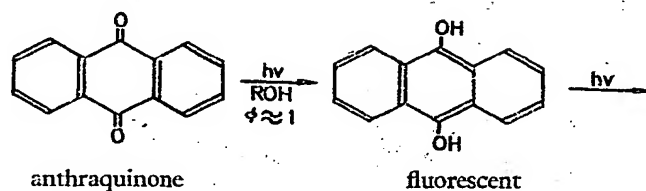


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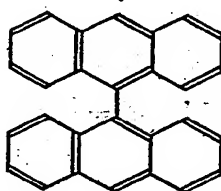
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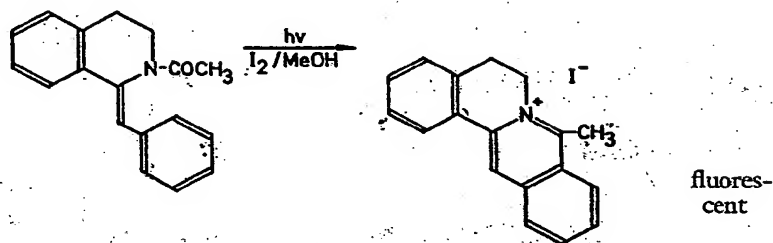
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D. M. Hercules,  
Fluorescence  
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p. 37

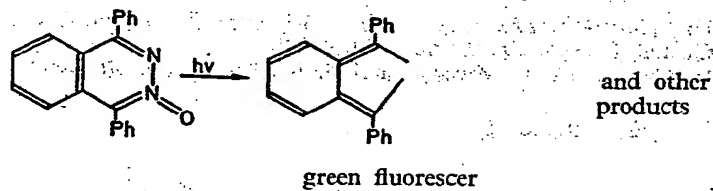


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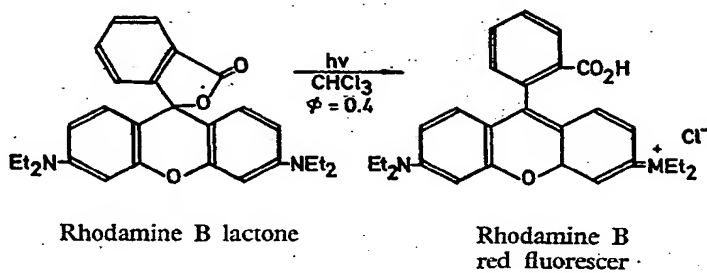
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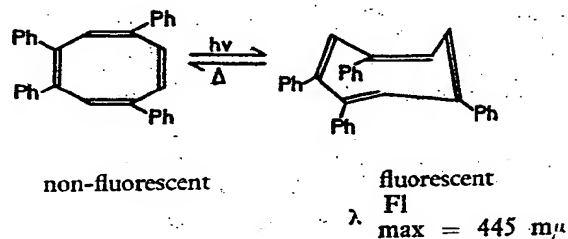
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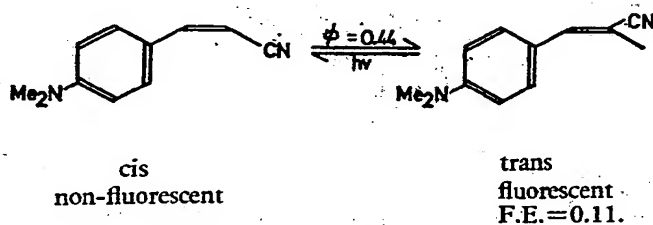
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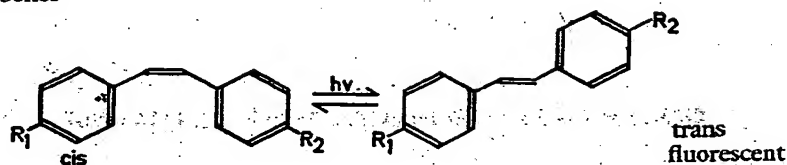
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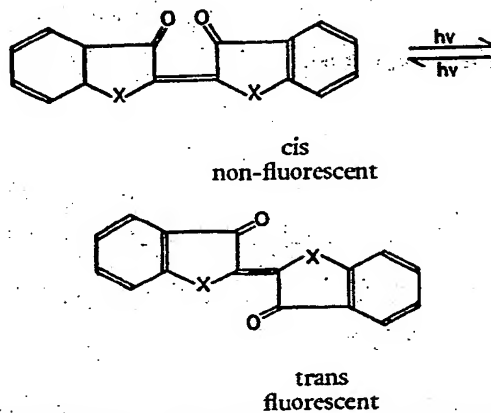
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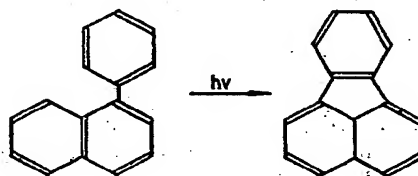
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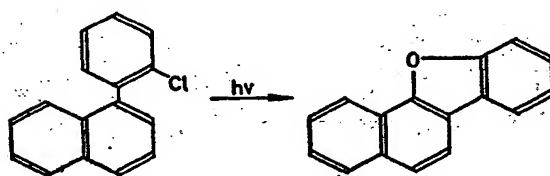
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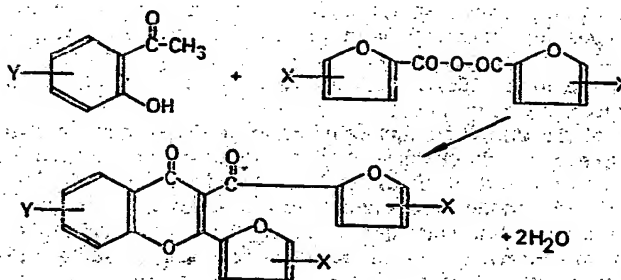
blue fluorescer

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W. A. Henderson and A. Zweig, Tetra, Letters 625 (1969).

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The compounds of Formula I in which Z is oxygen and R is a furyl group are preferably prepared by reacting an ortho-hydroxy acetophenone with a 2-furoic acid anhydride by the following reaction:



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In these compounds X and Y are defined in Formula I; either an unsubstituted or substituted pyromucic acid anhydride may be used or an acetyltohuol or other nuclear acidulated benzol may be employed, or both. When a dihydroxyacetophenone is used together with sufficient furoic acid compound, a furoxyloxy-substituted chromone is obtained directly, as is shown in Example 9.

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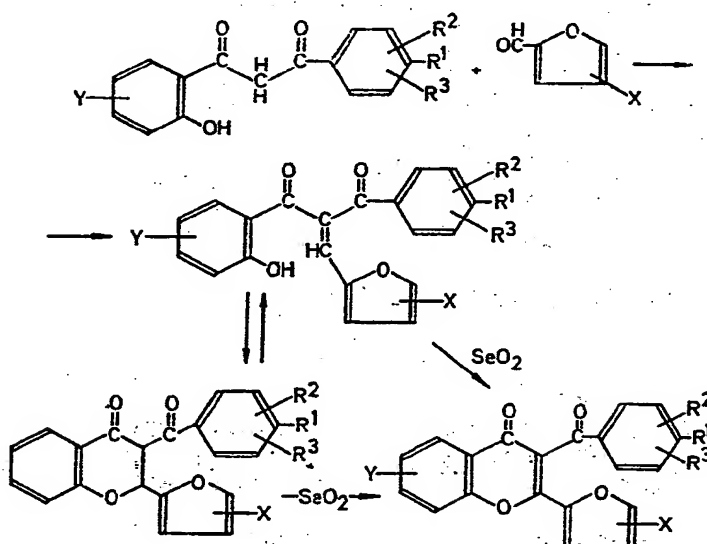
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The compounds of Formula I wherein R is a phenyl or substituted phenyl radical are most easily prepared by a two-step process of the type described in Examples 1, 2, 4 and 5. In the first step a furan aldehyde such as furfural, 5-methylfurfural or other lower alkyl-substituted furfural or a corresponding thiophene aldehyde such as alpha-thiophenylaldehyde is condensed with an equimolecular quantity of an ortho-hydroxy dibenzoylmethane to produce the corresponding trisubstituted 1,3-propanedione or the tautomeric *trans*-3-aroxy-2-(2-furyl)-4-chromanone. In the second step this is converted to a chromone by oxidation with selenium dioxide:

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The symbols X and Y are as previously defined, and R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are hydrogen, lower alkyl or lower alkoxy. It is understood that in all of these formulas the terms "lower alkyl" and "lower alkoxy" are intended to define alkyl radicals of from one to about six carbon atoms.

Ultraviolet irradiation of any of these chromones results in the generation of a colored compound which exhibits intense green fluorescence when observed in visible light. The spectral properties of all of the irradiated products are consistent with the furo chromone structure shown in Example 3; the presence, however, of a free hydroxy group at the 5-position interferes with the conversion. This was shown when 3-(2-furyl)-2-(2-furyl)-5-hydroxychromone was prepared (by refluxing the ester of Example 9 with concentrated hydrochloric acid) and irradiated with ultraviolet light. No color or fluorescent product was obtained.

Irradiation of the thiophene analog of Example 6 produced a compound generating a green fluorescence which changes to blue upon further irradiation. The methyl-substituted furyl compound of Example 4 exhibited similar behavior. It will be seen, therefore, that the chromone compounds form a series wherein the spectral properties are qualitatively similar but vary quantitatively from one compound to another. For this reason they can be made into an alphabet for use in coding and storing information that will be recovered rapidly and accurately by measuring quantitatively their response to irradiation with light having a suitable wavelength.

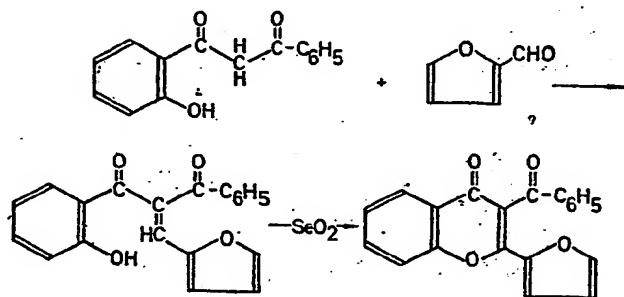
The following Examples disclose a wide range of compounds suitable as fluorescence precursor substances and in some cases the preparation of these. Many examples also illustrate the applicability of these substances to the method of recording and retrieving information as claimed. Some Examples up to Example 26 disclose conversion to a fluorescent compound by irradiation of a solution such as Example 16 or multi-step chemical procedures as in Example 3 for instance, but these disclosures are included for information only and are not intended to correspond to the method of the present invention.

#### Example 1

##### 3-Benzoyl-2-2(2-furyl) chromone

An intermediate compound, 2-furfurylidene-1-(o-hydroxyphenyl)-3-phenyl-1,3-propanedione is first prepared by condensing o-hydroxy-dibenzoylmethane with furfural. The intermediate may then be oxidized directly to the final product with selenium dioxide. The reactions are:





The o-hydroxy-dibenzoylmethane is prepared from o-benzoyloxyacetophenone as described in "Organic Syntheses", Vol. 32 (1952) page 74. A solution of 0.01 gram mole of this material, 0.011 gram ml. of furfural and several drops of piperidine in 50 mol of ethanol was refluxed for about one hour. The product which separated upon cooling was recrystallized from ethanol.

Calculated for  $C_{20}H_{14}O_4$ ; C, 75.46; H, 4.43

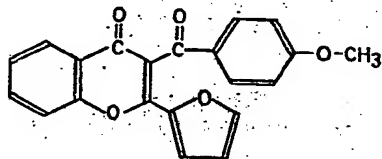
Found: C, 75.49; H, 4.45.

A mixture of 320 mg. of this material and 220 mg. of selenium dioxide in 10 ml. of dioxane was refluxed for 6 hours, filtered, and the filtrate evaporated to dryness. The resulting solid was recrystallized from ethanol to give 310 mg. (97% yield) of 3-benzoyl-2-(2-furyl) chromone melting at  $214.5-215^\circ\text{C}$ .

This product is both colorless and non-fluorescent. However, it is rearranged into a yellow colored compound which on further irradiation with visible light exhibits intense green fluorescence when its dilute solutions in methylene chloride are irradiated with U.V. light of 250—380 millimicron.

#### Example 2

##### 3-(p-Anisoyl)-2-(2-furyl) chromone



The intermediate compound *trans*-3-(p-anisoyl)-2-(2-furyl)-4-chromanone is first prepared and is oxidized with selenium dioxide.

A solution in ethanol of 0.01 gram mol of o-hydroxy-p'-methoxydibenzoylmethane (W. Baker and F. Glockling, J. Chem. Soc., 1950, p. 2761) and 0.011 gram mol of furfural was refluxed for one hour and cooled and the product was recrystallized from a methanol-water mixture. A 59% yield of tan crystals was obtained melting at  $136.5-140^\circ\text{C}$ .

Analysis: Calculated for  $C_{21}H_{16}O_5$ : C, 72.40; H, 4.63. Found: C, 72.39; H, 4.64.

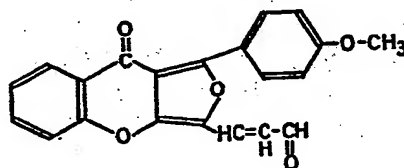
330 mg. of selenium dioxide was stirred into a solution of 480 mg. of this product in 15 ml. of dioxane and the mixture was refluxed for 6 hours. The product 3-(p-anisoyl)-2-(2-furyl) chromone, was obtained in 83% yield. Recrystallization from ethanol afforded cream colored crystals with a double m.p. of  $144-6^\circ\text{C}$ . and  $172.5-173.5^\circ\text{C}$ .

#### Example 3

##### Photolysis of 3-(p-anisoyl)-2-(2-furyl) chromone

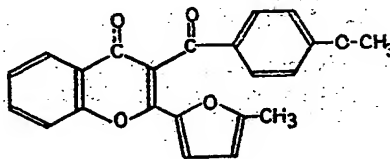
A solution of 16 mg. of the product of Example 2 in 900 ml. of methylene chloride in a quartz vessel was flushed with nitrogen for 30 minutes, stoppered, and irradiated in a reactor equipped with sixteen bulbs having a peak light emission at 313 millimicrons. After 1.25 hours irradiation the solution was concentrated in vacuo and combined with the product solutions of other similar runs. The combined solutions were evaporated to near dryness, taken up in a 9:1 mixture of petroleum ether and ether, and chromatographed over a silica gel column. This was eluted with petroleum ether-ether mixtures containing progressively more diethyl ether. A series of intermediate

fractions were combined, the solvent evaporated, and the residue was crystallized from a methylene chloride-cyclohexane mixture. It was a yellow-orange solid that fluoresced strongly in ultraviolet light. Analysis showed it to be a substituted furo (3,4-*b*) chromone of the formula:



#### Example 4

#### 3-(*p*-Anisoyl)-2-(5-methyl-2-furyl) chromone



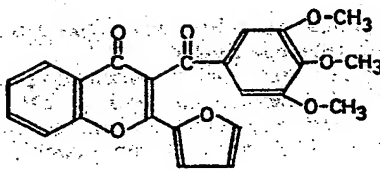
Equimolecular quantities of *o*-hydroxy-*p*'-methoxydibenzoylmethane and 5-methylfurfural were reacted by the procedure described in Example 2. The product, *trans*-3-(*p*-anisoyl)-2-(5-methyl-2-furyl) 4-chromanone was obtained in 81% yield. The purified product consisted of pale yellow needles melting at 137–140°C.

A mixture of 1.81 grams of this product and 0.61 grams of selenium dioxide in 40 ml. of dioxane was refluxed for 6 hours to give 1.51 grams of 3-(*p*-anisoyl)-2-(5-methyl-2-furyl) chromone melting at 167–169°C.

Analysis: Calculated for  $C_{22}H_{18}O_5$ : C, 73.32; H, 4.48. Found: C, 73.25; H, 4.35.

#### Example 5

#### 3-(3,4,5-Trimethoxybenzoyl)-2-(2-furyl) chromone

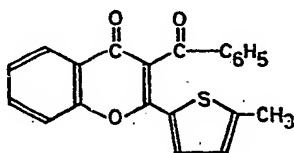


A solution of 0.01 gram mole of 2-hydroxy-3',4',5'-trimethoxy-dibenzoylmethane (J. Chem. Soc. 1950, page 2762) and 0.011 gram mole of furfural in 50 ml. of ethanol was refluxed for one hour. The product, obtained in 65% yield, was recrystallized from ethanol. It was obtained as a mixture of crystalline modifications which, after further recrystallizations, melted at 129–145°C. The product was identified as *trans*-3-(3,4,5-trimethoxybenzoyl)-2-(2-furyl)-4-chromanone.

A sample of this material was dissolved in dioxane and oxidized with selenium dioxide as described in Example 1. The oxidation product, 3-(3,4,5-trimethoxybenzoyl)-2-(2-furyl) chromone, was obtained as colorless crystals in a 94% yield. They melted at 161–162°C.

Analysis: Calculated for  $C_{23}H_{18}O_7$ : C, 67.97; H, 4.46. Found: C, 68.14; H, 4.47.

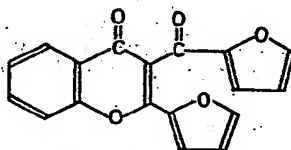
## Example 6

*3-Benzoyl-2-(5-methyl-2-thienyl) chromone*

This thiophene analog was prepared by the procedure of Example 2. A solution of 0.1 gram moles of o-hydroxy-dibenzoylmethane and 0.11 gram moles of 5-methyl-2-thiophenecarboxaldehyde in 80 ml. of ethanol was refluxed for about one hour. The product, *trans*-3-benzoyl-2-(5-methyl-2-thienyl)-4-chromanone was obtained in 43% yield. It melted at 147—149°C. Upon oxidation with selenium dioxide in dioxane the 3-benzoyl-2-(5-methyl-2-thienyl) chromone product was obtained in 80% yield. One crystallization from a dioxane-ethanol mixture afforded colorless crystals melting at 187—188.5°C.

Analysis: Calculated for  $C_{21}H_{14}O_3S$ : C, 72.81; H, 4.07; S, 9.26. Found: C, 72.67; H, 3.66; S, 9.25.

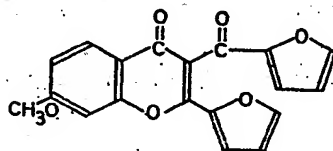
## Example 7

*3-(2-Furoyl)-2-(2-furyl) chromone*

A mixture of 0.68 grams (0.005 mole) of o-hydroxyacetophenone, 4.95 grams (0.024 mole) of 2-furoic anhydride (J.A.C.S. 71, 2242) and 1.5 gram (0.015 mole) of triethylamine was heated at 175—180°C. for 5 hours. The resulting black oil was cooled and suspended in a 1:1 methylene chloride-ether mixture and the insoluble material was removed by filtration. The filtrate was washed twice with 5%  $Na_2CO_3$  solution, dried, and evaporated and a second crop was recovered in the same manner. One recrystallization of the combined crops from ethanol gave 0.83 grams of 3-(2-furoyl)-2-(2-furyl) chromone. When this was dissolved in methanol, treated with decolorizing carbon and again recrystallized a purified product was obtained as tan crystals melting at 214—215°C.

Analysis: Calculated for  $C_{18}H_{10}O_6$ : C, 70.59; H, 3.29. Found: C, 70.73; H, 3.37.

## Example 8

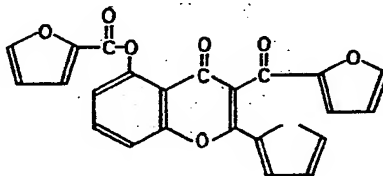
*3-(2-Furoyl)-2-(2-furyl)-7-methoxychromone*

A mixture of 0.83 grams of o-hydroxy-p-methoxyacetophenone, 4.1 grams of 2-furoic anhydride and 1.5 grams of triethylamine was heated at 150°C. for 6 hours and worked up as in Example 7. The 3-(2-furoyl)-2-(2-furyl)-7-methoxychromone was obtained as a tan solid melting at 234—235°C.

Analysis: Calculated for  $C_{19}H_{12}O_6$ : C, 67.85; H, 3.60. Found: C, 67.37; H, 3.67.

## Example 9

## 3-(2-Furoyl)-2-(2-furyl)-5-(2-furoyloxy) chromone



A mixture of 0.75 grams of 2,6-dihydroxyacetophenone, 5 grams of 2-furoic anhydride and 1.5 grams of triethylamine was heated at 160°C. for 4 hours. The resulting black solid mass was triturated with a 2:1 mixture of methylene chloride and ether. There was recovered 1.85 grams (89% yield) of 3-(2-furoyl)-2-(2-furyl)-5-(2-furoyloxy) chromone as light brown crystals melting at 252—253°C.

Analysis: Calculated for  $C_{23}H_{12}O_8$ : C, 66.35; H, 2.91. Found: C, 66.70; H, 2.98.

## Example 10

This example shows the method for condensation of aldehydes with *o*-hydroxydibenzoylmethanes. In the general procedure, 2-furfurylidene-1-(*o*-hydroxyphenyl)-3-phenyl-1,3-propanedione; trans-3-(*p*-anisoyl)-2-(2-furyl)-4-chromanone; trans-3-(3,4,5-trimethoxybenzoyl)-2-(2-furyl)-4-chromanone; and trans-3-(*p*-anisoyl)-2-(5-methyl-2-furyl)-4-chromanone were prepared following the method of Baker and Glockling, J. Chem. Soc., 2579 (1962). This is the method used in Examples 10a, 10b, 10c and 10d relating to the preparation of intermediate products in the synthesis of precursor substances as in Examples 11 and 12 for example. A solution of 0.010 mole of the *o*-hydroxydibenzoylmethane, 0.011 mole of the aldehyde, and several drops of piperidine in 50 ml. of ethanol was refluxed for 30 minutes to 2 hours. The product which separated upon cooling was recrystallized from ethanol.

## Example 10a

2-Furylfurylidene-1-(*o*-Hydroxyphenyl)-3-phenyl-1,3-propanedione

Reaction of *o*-hydroxydibenzoylmethane with furfural afforded an 80% yield of 10a, mp 154.5—159°C.

Anal. Calcd. for  $C_{20}H_{14}O_4$ : C, 75.46; H, 4.43. Found: C, 75.49; H, 4.45.

## Example 10b

Trans-3-(*p*-Anisoyl)-2-(2-furyl)-4-chromanone

*o*-Hydroxy-*p*'-methoxydibenzoylmethane and furfural gave this compound in 59% yield, mp 127—130°C. Recrystallization from methanol-water afforded tan crystals, mp 136.5—140°C. The nuclear magnetic resonance spectrum showed the aliphatic ring protons as a pair of doublets centered at  $\tau$  3.94 and  $\tau$  4.72 ( $J=10.5$  Hz).

Anal. Calcd. for  $C_{21}H_{16}O_5$ : C, 72.40; H, 4.63. Found: C, 72.39; H, 4.64.

## Example 10c

## Trans-3-(3,4,5-Trimethoxybenzoyl)-2-(2-furyl)-4-chromanone

This compound was obtained from 2-hydroxy-3',4',5'-trimethoxydibenzoylmethane and furfural. The yield was 65%, mp 114—115.5°C. Recrystallization from ethanol gave a mixture of crystalline modifications, mp 113—143°C. Two further recrystallizations raised the mp to 129—145°C.

Anal. Calcd. for  $C_{23}H_{20}O_7$ : C, 67.64; H, 4.94. Found: C, 67.91; H, 4.96.

Solution infrared spectra ( $CHCl_3$ ) of the low and high melting samples were identical.

## Example 10d

Trans-3-(*p*-Anisoyl)-2-(5-methyl-2-furyl)-4-chromanone

This compound was obtained from *o*-hydroxy-*p*'-methoxydibenzoylmethane and 5-methylfurfural in 81% yield; mp 134—136.5°C. The analytical sample separated as pale yellow needles, mp 137—140°C.

Anal. Calcd. for  $C_{22}H_{18}O_5$ : C, 72.92; H, 5.01. Found: C, 72.98; H, 4.94.

## Example 11

*3-(3,4,5-Trimethoxybenzoyl)-2-(2-furyl)chromone*

Oxidation of the compound of Example 10c afforded a 94% yield of 3-(3,4,5-trimethoxybenzoyl)-2-(2-furyl)chromone, mp 160—161.5°C. The analytical sample was obtained as colorless crystals, mp 161—162°C., from ethanol.

Anal. Calcd. for  $C_{23}H_{18}O_7$ : C, 67.97; H, 4.46. Found: C, 68.14; H, 4.47.

## Example 12

*3-(p-Anisoyl)-2-(5-methyl-2-furyl)chromone*

A mixture of 1.81 g. of the compound of Example 10d and 0.61 g of selenium dioxide in 40 ml. of dioxane was refluxed for 6 hours to give 1.51 g. (84%) of 3-(p-anisoyl)-2-(5-methyl-2-furyl)chromone, mp. 167—169°C.

Anal. Calcd. for  $C_{22}H_{16}O_5$ : C, 73.32; H, 4.48. Found: C, 73.25; H, 4.35.

## Example 13

*3-(2-Furoyl)-2-(2-furyl)chromone*

A mixture of 0.68 g. (0.005 mole) of *o*-hydroxyacetophenone, 4.95 g. (0.024 mole) of 2-furoic anhydride, and 1.5 g. (0.015 mole) of triethylamine was heated at 175—180°C. for 5 hours. The cooled black oil was treated with 1:1 methylene chloride-ether and the insoluble product was filtered. The filtrate was washed twice with 5%  $Na_2CO_3$ , dried, and evaporated and a second crop was crystallized in the same manner. One recrystallization of the combined crops from ethanol gave 0.83 g. (54%) of 3-(2-furoyl)-2-(2-furyl)chromone, mp 212—213°C. A second recrystallization from methanol using charcoal afforded tan crystals, mp 214—215°C.

Anal. Calcd. for  $C_{18}H_{10}O_5$ : C, 70.59; H, 3.29. Found: C, 70.73; H, 3.37.

## Example 14

*3-(2-Furoyl)-2-(2-furyl)-7-methoxychromone*

A mixture of 0.83 g. of *o*-hydroxy-*p*-methoxyacetophenone, 4.1 g. of 2-furoic anhydride, and 1.5 g. of triethylamine was heated at 150°C. for 6 hours and worked up as in the preceding example. 3-(2-furoyl)-2-(2-furyl)-7-methoxychromone was obtained as a tan solid; 0.36 g. (21%), mp 234—235°C.

Anal. Calcd. for  $C_{19}H_{12}O_6$ : C, 67.85; H, 3.60. Found: C, 67.37; H, 3.67.

## Example 15

*3-(2-Furoyl)-5-(2-furoyloxy)-2-(2-furyl)chromone*

A mixture of 0.75 g. of 2,6-dihydroxyacetophenone, 5.0 g. of 2-furoic anhydride, and 1.5 g. of triethylamine was heated at 160°C. for 4 hours. The resulting black solid mass was triturated with 2:1 methylene chloride-ether to give 1.85 g. (89%) of 3-(2-furoyl)-5-(2-furoyloxy)-2-(2-furyl)chromone as light brown crystals, mp 252—253°C. Trituration with boiling methanol gave tan crystals of the same mp; 5.99, 6.12  $\mu$ .

Anal. Calcd. for  $C_{23}H_{12}O_8$ : C, 66.35; H, 2.91. Found: C, 66.70; H, 2.98.

## Example 16

Ultraviolet irradiation of dilute solutions in methylene chloride of the chromones of Examples 1—2 and 5—9 resulted in progressive generation of yellow colors, which products exhibited intense green fluorescence when subsequently irradiated with visible light. This solvent was also substituted by others such as methanol, acetonitrile and benzene with essentially equivalent results. The solutions of the chromones, approximately  $5 \times 10^{-3}$  M, were irradiated with 240—400 m $\mu$  light from a 1000 watt high pressure mercury arc.

## Example 17

A  $10^{-2}$ N solution of 1-*o*-chlorophenylnaphthalene in benzene was irradiated with a 3130 A Hanovia 100 watt lamp with Corning #9863 and potassium chromate filter. The irradiated product was fluoranthene which gave a blue fluorescence on further irradiation in the visible spectrum.

## Example 18

*o-Chlorophenyl-1-naphthyl Ether*

In a 3-neck flask were mixed 95 g. (0.75 mole) of *o*-chlorophenol and 35 g. (0.75 mole) of pulverized potassium hydroxide. The mixture was stirred under nitrogen at 150 until the base was dissolved. The mixture was cooled, and to it was added 100 g. (0.50 mole) of  $\alpha$ -bromonaphthalene and 1.2 g. of activated copper bronze (United States

Bronze Powder Works C—118 bronze powder). The whole was stirred vigorously under nitrogen and slowly heated to 190°C. at which temperature about 20 ml of water was distilled off. The mixture was further heated at 210°C. for 2 hours. Workup by extraction with aqueous potassium hydroxide and then water followed by distillation gave 14.7 g. (16%) of *o*-chlorophenyl-1-naphthyl ether as a viscous, almost colorless, non-fluorescent oil, b.p. 138—140°/0.04 mm. A small sample was further purified by g.l.c. for analysis.

Anal. Calcd. for  $C_{16}H_{11}OCl$ : C, 75.46; H, 4.35; mol. wt. 254. Found: C, 75.83; H, 4.41; m/e 254.

#### Example 19

##### *o*-Chlorophenyl-1-naphthyl Ether

A solution of 200 mg. of *o*-chlorophenyl-1-naphthyl ether as obtained in Example 18, in 300 ml. of benzene, was bubbled with nitrogen in a quartz vessel. The solution was then irradiated with 254 m $\mu$  light in a Rayonet reactor for 18 hours. The resulting yellow solution was evaporated and the residue chromatographed on alumina. The appropriate fractions (110 mg., 65%) were combined, sublimed, and recrystallized 3 times from hexane and once from methanol to give 55 mg. (32%) of benzo[b]naphtho-[2,1-d]furan, mp 102—103 (Liter. 103). This compound gave a blue fluorescence on further irradiation with u.v. light of longer wavelength.

##### Determination of Yield and Quantum Yield

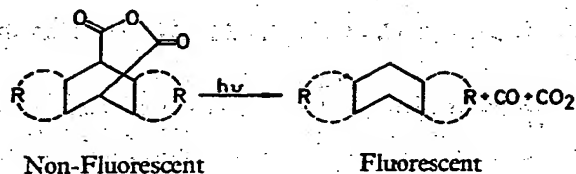
A solution of 25.5 mg. of *o*-chlorophenyl-1-naphthyl ether in 10 ml. of benzene was irradiated in a 1 cm ultraviolet quartz cell with 313 m $\mu$  light of known intensity. The rate of formation of benzo[b]-[2,1-d]furan was followed by observing the appearance of its long wavelength peak at 340 m $\mu$ . The quantum yield calculated therefrom was  $3.2 \times 10^{-3}$ .

A portion of the above solution diluted to 1/100 was irradiated in the same cell for 18 hours with 300 m $\mu$  light. The yield of benzo[b]-2[2,1-d]furan calculated from the size of the 340 m $\mu$  peak was 70%.

#### Example 20

The compound of Example 2 was irradiated with 3130 Å light in solutions of methylene chloride, benzene and acetonitrile at concentrations from  $10^{-2}$  to  $10^{-4}$ M. A product which exhibited fluorescence in visible light was formed. A detectable fluorescence is present after less than a second and the density increases with the time of exposure to ultraviolet light.

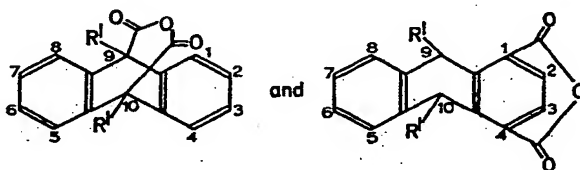
A particularly valuable class of fluorescer precursor compounds which may be used herein are polycyclic aromatic anhydrides which undergo a photochemical decarboxylation and decarbonylation in accordance with the following equation:



where R represents an aromatic residue, i.e., the structure which together with the nucleus will form an aromatic compound, or hydrogen atoms, wherein there are preferably three rings in the polycyclic aromatic compound.

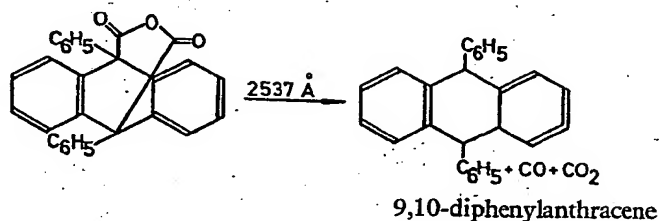
This same reaction takes place when such compounds are raised to their melting point, since they decompose at that point.

Anhydrides which are within the scope of this group of compounds may be represented by the formula;



where exemplary substituents R' are phenyl, p-anisyl, p-cyanophenyl, phenylethynyl, p-phenylphenyl, and 1-naphthyl. In addition, a benzo-substituent may be present at 1—2 or 6—7; or 1—2 and 5—6; or 2—3; or 2—3 and 7—8. Methyl or methoxy substituents may be present at 1 and 2 or 1, 2, 7 and 8 or corresponding positions. Other lower alkyl or alkoxy substituents may also be used.

In particular, the 9—10, anhydride of 9,10-diphenylanthracene undergoes this reaction as follows:



Under 3,000 Å light, 9,10-diphenylanthracene fluoresces. The same reduction occurs with the 1,4-anhydride of 9,10-diphenylanthracene.

The following examples will illustrate preparation and use of the anhydrides of polycyclic aromatic as fluorescer precursors.

#### Example 21

In this example, 9,10-diphenyl-9,10-dihydroanthracene-9,10-anhydride, which does not fluoresce, was photochemically converted to 9,10-diphenylanthracene, a blue fluorescent compound.

A sample of 9,10-diphenyl-9,10-dihydroanthracene-9,10-anhydride, prepared as described by M. M. Rauhut, D. Sheehan, R. A. Clark and A. M. Semsel, *Photochemistry and photobiology* (1965) Vol. 4, pp. 1,097—1,110, having a melting point 223—225° C. (decomposition), was dissolved in methylene chloride. No fluorescence was evident when irradiated with long ultraviolet light of 300 mμ or greater. The solution was flushed with nitrogen and irradiated with ultraviolet light from a B—H6 lamp (principally less than 300 mμ). After a few minutes, a strong blue fluorescence was detectable under long wave ultraviolet light without further conversion of anhydride. Comparison of the fluorescent material with the spectrum of an authentic sample confirmed that the fluorescent product was 9,10-diphenylanthracene.

#### Example 22

A sample of the anhydride of Example 21 was recrystallized from methylene chloride-petroleum ether to give a mixture of hard prisms and soft fluffy solid. The prisms were separated and had a melting point of 243—248° C. They appeared to be a purer form of the anhydride.

A  $1.1 \times 10^{-4}M$  solution in methylene chloride was irradiated with short wave ultraviolet light from a B—H6 lamp as in Example 21. Strong blue fluorescence could be detected after a few seconds by long wave ultraviolet irradiation as in Example 21 without further conversion of the anhydride.

#### Example 23

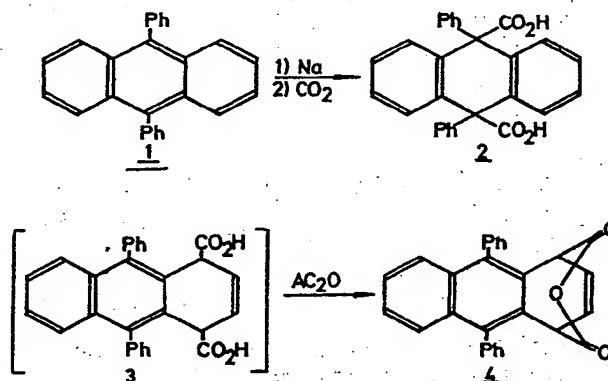
In the same manner as in Examples 21 and 22, fluorescence was obtained by photoconversion of the anthracene—9,10-anhydride to anthracene.

#### Example 24

Fluorescence was also obtained from the anhydrides of Examples 21 and 22, by the application of heat to decompose the anhydride. The anhydrides decompose at the melting point to the corresponding anthracene compound. Heat was supplied in either the form of infrared radiation or a hot stamp directly applied to the anhydride.

## Example 25

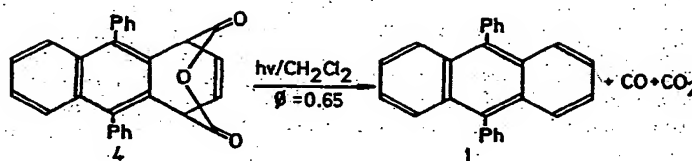
## Preparation of 9,10-Diphenyl-1,4-dihydroanthracene-1,4-anhydride



The methylene chloride solution obtained from the trituration of 2 was evaporated to a gum containing 3 which was dissolved in the minimum amount of acetic anhydride. The solution was refluxed for 20 minutes and distilled to dryness *in vacuo*. The dark red residue was crystallized from methylene chloride-petroleum ether to give a 2.5% yield (based on 1) of 4, m.p. 247—265°C. dec. Recrystallization from the same solvent mixture afforded nearly colorless crystals, m.p. 263—271°C. dec.

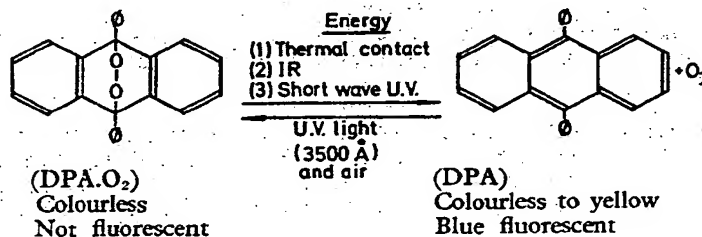
Anal. Calcd. for  $C_{28}H_{18}O_3$ : C, 83.56; H, 4.51. Found: C, 83.58; H, 4.77.

## Example 26



A methylene chloride solution of the compound of Example 25 was irradiated by a shortwave ultraviolet light source as in Example 21. Strong blue fluorescence could be detected after a few seconds by irradiation with a long wave ultraviolet light as in Example 21 without further conversion of the anhydride.

Certain endoperoxides may be used as the fluorescer precursor substance, as illustrated by the following equation, using 9,10-diphenyl anthracene endoperoxide as an example:



Also, some endoperoxides are weakly fluorescent, but on irradiation images are formed which are strongly fluorescent and readily detectable under suitable long wave ultraviolet radiation and may or may not be visible. The process is also reversible, so that the fluorescent image may be erased, and a new image formed. This cycle may be performed any number of times.



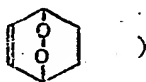
The requisite energy for the conversion of the endoperoxides and formation of images may be applied in different ways. It may be done by the physical contact of a hot die to the substrate incorporating the endoperoxide. In this instance, the die will have the shape of the desired image. A temperature of from 20°C. to 200°C., preferably 150°C. to 200°C., is suitable. Images can be produced in from 1 to 3 seconds at higher temperatures. The time and temperature will be variable depending on the substrate material and effect desired.

The substrate could also be irradiated by an imagewise pattern of infrared radiation, or short wave ultraviolet radiation of about 2,000 to 3,000 Å wavelength. Energies of about 0.07 joules/cm<sup>2</sup> have been found adequate. The radiant source may be of various types providing ultraviolet or infrared-radiation, including lamps, electric arcs, or ultraviolet and infrared lasers. The image can be formed in any well-known manner as by projecting a beam through a stencil, by use of moving mirror systems with lasers and the like. When infrared radiation is used, it is advantageous to incorporate infrared-absorbing agents such as charcoal, or chemical absorbers, with the aromatic polycyclic imaging compounds.

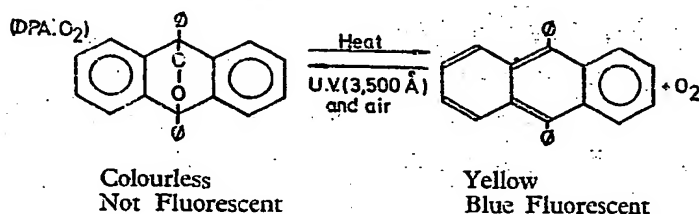
For reversing the process and erasing the image, the aromatic compound is irradiated with long wave ultraviolet light, most advantageously of 3,500 Å wavelength, in the presence of air or oxygen to cause conversion of the aromatic compound to the original endoperoxide.

In general, any compound capable of forming an endoperoxide will work in this system as long as this endoperoxide is decomposable under the types of energy previously discussed, to a fluorescent product.

Some of the names used in the literature to describe these cyclic peroxides include: transannular peroxides, 1,4-peroxides, photo-oxides, photo-peroxides, transannular epidioxides, 1,4-epiperoxides, aromatic peroxides (with or without numbers to indicate the positions involved, i.e., 9,10-dimethyl-anthracene-9,10-peroxide or 9,10-dimethyl-anthracene peroxide, also rubrene peroxide), endoperoxides (or endoperoxides, (also with or without numbers, i.e., 9,10-diphenylanthracene-9,10-endoperoxide or 9,10-diphenylanthracene endoperoxide) and dioxabicyclo systems (i.e., 5,6-dioxabicyclo-[2.2.2.]octene-2:



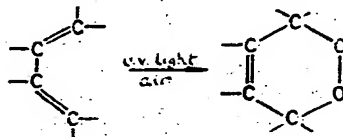
For the reversible system, the heat generated image can be converted back to the endoperoxide. This is usually accomplished by U.V. light and air. Using 9,10-diphenylanthracene endoperoxide as an example, the reactions are:



For the irreversible system, the heat generated image cannot be converted back to the starting endoperoxide. Thus, the image produced by heating the endoperoxide may be an oxidation product (quinone, etc.) or other fluorescent decomposition product not capable of being converted to colorless and non-fluorescent material. Also, a normally reversible system can be made irreversible by preventing oxygen from reacting with the aromatic (see Table I).

The initial endoperoxide may be prepared by using U.V. light in the presence of air or oxygen (with or without a sensitizer), chemical synthesis, or with active oxygen prepared by electrodeless discharge.

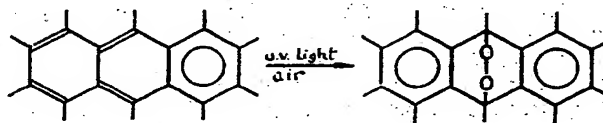
A variety of compounds containing a 1,3-diene structure are known to give peroxides under irradiation with u.v. light in air:



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The most useful class of compounds for this invention is the aromatic acenes and their derivatives (i.e., anthracene, naphthacene, pentacene, hexacene, etc.).

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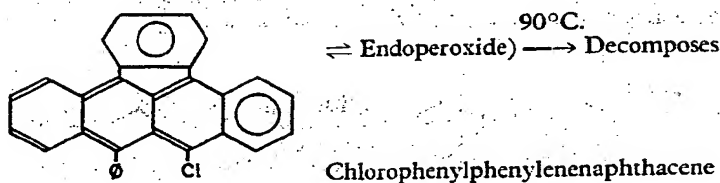
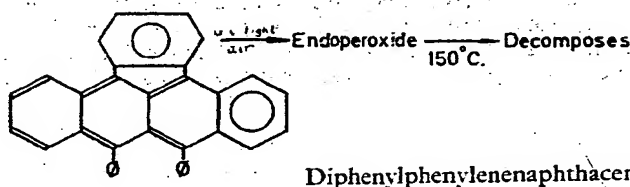


Additional aromatic endoperoxides within the scope of this invention are disclosed in "Organic Chemistry, A Series of Monographs", Vol. 8, J. Hamer, ed., 1967, p. 229:

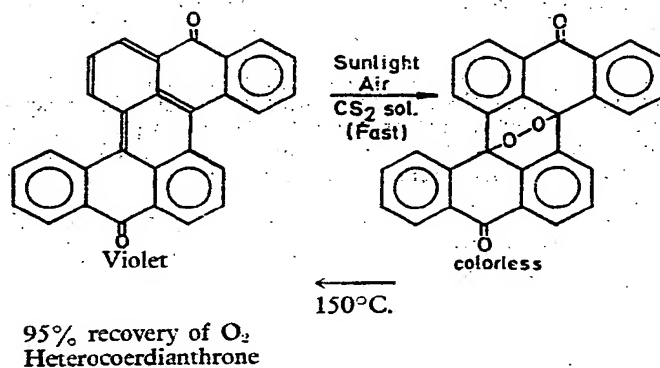
10

Larger polynuclear aromatic endoperoxides are known as follows:

10



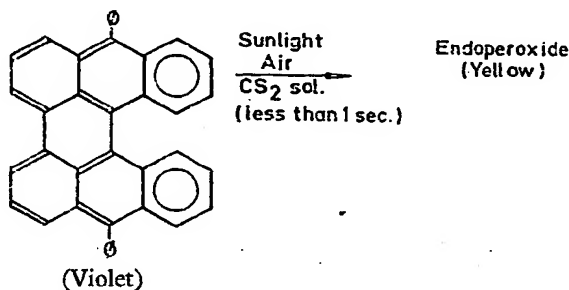
C. Dufraisse and M. T. Mellier, Compt. rend., 215, 576 (1942).



15

C. Dufraisse and M. T. Mellier, Compt. rend., 215, 541 (1942).

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p. 238; E. G. E. Hawkins "Organic Peroxides, Their Formation and Reactions", E. and F. F. Spon Ltd., London, 1961.

Other polycyclic hydrocarbons that can be converted to non-fluorescent endoperoxides are: 1,2-benzoanthracenes, rubrene, naphthacene, 9,10-diphenylnaphthacene, 1,2,3,4-tetrahydro-9,10-diphenylnaphthacene, 9,11-diphenyl-10,12-bis-(biphenyl)naphthacene, 2,6,10,12-tetraphenyl-9,11-bis(biphenyl)naphthacene, 8,9-dibenzpentalene, heterocoerdianthrone, and the three isomeric p-tolyl-tetraphenylcyclopentadienols.

Other derivatives of polycyclic aromatic compounds may be useful provided they have an oxidized and a reduced state and are fluorescent in one such state, and are capable of being changed from one state to the other by the application of suitable energy. By oxidized and reduced state is meant a polycyclic aromatic compound having at least one ring with a diene structure which is capable of being converted to a monoene structure by 1,4 addition to the ring. The endoperoxides of anthracene are illustrative, as previously pointed out. In addition, halogen derivatives of anthracene would also be applicable, for example.

The following further examples are given to illustrate the polycyclic aromatic type of compounds.

#### Example 27

The 9,10-diphenylanthracene endoperoxide (DPA.O<sub>2</sub>) was prepared from commercially available 9,10-diphenylanthracene (DPA) as follows:

##### 9,10-Diphenylanthracene Endoperoxide

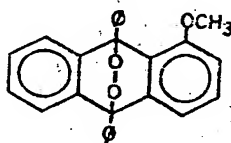
Potassium hydroxide (12 g.) was added slowly (1/2 hour) to 37 ml. of 30% hydrogen peroxide with stirring at 0° C. (ice-water bath). A solution of 1.01 g. (3 mM) 9,10-diphenylanthracene in 50 ml. chlorobenzene was added to the reaction vessel. The mixture was stirred gently, so that the boundary between the two liquid phases was not broken and bromine (5 ml.) in chloroform (5 ml.) was added to the lower (aqueous-KOH-H<sub>2</sub>O<sub>2</sub>) phase through a capillary tube during a period of 4 hours. The organic phase was separated from the aqueous phase and washed with water. The organic solution was concentrated under reduced pressure to a yellow mud. This material was chromatographed on F-20 Alumina (eluted with 50:50 n-hexane:benzene). After recrystallization from n-hexane/benzene, 0.612 g. (55% yield) of 9,10-diphenylanthracene endoperoxide and 0.277 g. (27% recovered) 9,10-diphenylanthracene was obtained.

A solution of DPA.O<sub>2</sub> in an organic solvent (such as benzene) was allowed to dry on non-fluorescent paper to leave 0.05 mg. to 0.1 mg. of DPA.O<sub>2</sub> per square centimeter. An image was rapidly produced by applying a heated object of about 200° C. The images had no visible color but exhibited bright blue fluorescence under u.v. light. If too hot or too long a contact time was used, then the image was transferred to the underlying substrate (paper). Higher concentrations of DPA.O<sub>2</sub> gave images which were yellow colored and which exhibited blue fluorescence.

The images produced on paper coated with DPA.O<sub>2</sub> were bleached after 15 minutes to 1/2 hour exposure to 3,500 Å ultraviolet light in air (Rayonet Photochemical Reactor). Also some fading of the blue fluorescent images was observed after 4 days in the direct afternoon sunlight. New images were produced on the above papers by reapplying the heated objects. One treated paper was carried through six cycles.

In the remaining Examples, the fluorescent substances which are formed can be detected on subsequent exposure to ultraviolet radiation.

## Example 28

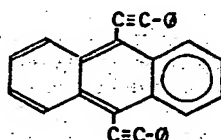


## 1-Methoxy-9,10-diphenylanthracene endoperoxide

This endoperoxide is described in C. Dufraisse, L. Velluz, R. Demuyne, *Compt. rend.*, 215, 111 (1942).

A benzene solution of this endoperoxide was allowed to dry on a piece of white, non-fluorescent paper to leave a colorless, non-fluorescent circle. Heated (150—200°C.) objects (i.e., keys, metal with raised letters, etc.) developed blue-green fluorescent material images (no visible color) when placed on the treated paper for less than a second. Higher temperatures or longer contact time caused the fluorescent (no visible color) images to be transferred to the material (paper) under the treated paper. These images were bleached in the Rayonet Photochemical Reactor at 3,500 Å in 15 minutes. No new images could be developed by heated objects in the areas where the first images were. Good images were formed in areas where no first images were.

## Example 29

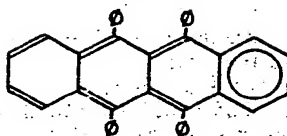


## 9,10-Bis(phenylethynyl)anthracene

A benzene solution of this compound was allowed to dry on a piece of white (non-fluorescent) paper to leave a slightly orange-colored and yellow-fluorescent circle. The endoperoxide was formed by irradiating the paper for 15 minutes in the Rayonet Photochemical Reactor at 3,500 Å. The yellow-green fluorescence was bleached but the paper was still slightly orange. Information was then recorded by means of heated (about 200° C.) objects (keys, etc.) placed on this paper which caused the development of yellow-colored and yellow-green fluorescent material images in about 1 second. The yellow-colored and yellow-green fluorescent material images were also transferred to ordinary paper by using longer contact time (2—4 seconds) or higher temperatures. These images could be bleached by 3,500 Å ultraviolet light but new images were difficult to produce on top of bleached images.

9,10-Bis(phenylethynyl)anthracene may be prepared as described by W. Ried, W. Donner and W. Schlegelmilch, *Ber.*, 94, 1051 (1961).

## Example 30



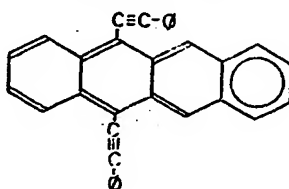
## Rubrene

A benzene solution of rubrene was allowed to dry on white, non-fluorescent paper to leave a pink-colored and orange fluorescent circle. The pink color and orange fluorescence was bleached in two minutes by ultraviolet irradiation (3,500 Å) in air (Rayonet Photochemical Reactor), thus forming the endoperoxide. Information was then recorded by means of heated (about 200° C.) objects (keys, etc.) placed on this bleached paper, a pink-colored and orange fluorescent material image forming in less than one second. These images were similarly bleached in a few minutes by ultraviolet irradiation

(3,500 Å) in air. Ordinary fluorescent laboratory light, also bleached the images slowly. The process was repeated three times on the same coated paper. Lower temperatures and/or shorter contact times of the heated objects produced only the orange fluorescent image (no visible color). These transformations can again be explained by the reversible formation of the endoperoxide.

Images were also transferred to an underlying substrate when hotter objects and/or longer contact times were used.

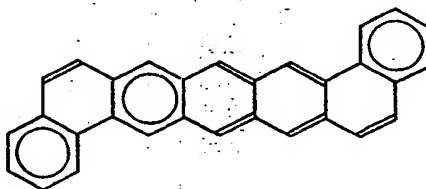
#### Example 31



#### 5,12-Bis(phenylethynyl)tetracene

A benzene solution of this compound was allowed to dry on a piece of white (non-fluorescent) paper to leave a dull gray and slightly orange fluorescent circle. Dilute concentrations of this compound on paper were almost colorless and slightly orange fluorescent. The endoperoxide was formed more easily on this paper since the orange fluorescence was bleached slowly in air by laboratory fluorescent light and more rapidly (5 to 10 minutes) in the Rayonet Photochemical Reactor at 3,500 Å. Information was then recorded by means of heated (about 200°C.) objects (keys, etc.) which rapidly (1—3 seconds) generated red visible colored and orange fluorescent material colored images on this paper. If lower temperature objects were used, then only the orange fluorescent material images were formed. These images were also transferred to untreated paper (as in the above cases) by using slightly hotter objects or longer contact time. The images were bleached in Rayonet Photochemical Reactor at 3,500 Å in 15 minutes. This was a reversible system since one treated paper was carried through six cycles.

#### Example 32



1,2,8,9-Dibenzpentalene, obtained commercially from L. Light & Co., Ltd., Colnbrook, England.

A benzene (or xylene) solution of this compound was allowed to dry on a piece of white, non-fluorescent paper to leave a colorless and non-fluorescent circle. Higher concentrations of the compound on paper were slightly purple colored and non-fluorescent. Ordinary fluorescent laboratory light caused formation of the non-fluorescent endoperoxide. The endoperoxides were also formed by ultraviolet radiation (3,500 Å, Rayonet) in 5 minutes. Information was then recorded by means of heated (about 200°C.) objects (keys, etc.) rapidly (1,3 seconds) which produced yellow fluorescent but normally invisible images. These images were bleached slowly by the fluorescent laboratory lights and in 5 minutes in the Rayonet Photochemical Reactor at 3,500 Å to form the endoperoxide again. Heated objects again formed the fluorescent images on this paper. As in the other cases, hotter objects or longer (2—4 seconds) contact time transferred the yellow fluorescent (no visible color) images to untreated paper or any substrate used under the treated paper.

Some results of Examples 27 to 32 are summarized in Table I below.

## Example 33

Other aromatic derivatives (in addition to the endoperoxide) may be useful for imaging by heat or ultraviolet light. Thus, an attempt to prepare the endoperoxide of BPEA (9,10-bis(phenylethynyl)anthracene) using the procedure described for DPAO<sub>2</sub> [E. McKeown and W. A. Waters, J. Chem. Soc., 1040B (1966)] gave a small amount of non-fluorescent material which had an infrared and mass spectrum indicating;

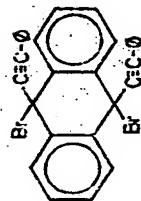


TABLE I

## Aromatic Endoperoxides on Paper

Endoperoxide of	Initial Appearance of Endoperoxide	Image Formed by Heat	Time for Bleaching by 3500Å U.V.
27 DPA	Colorless, Not Fluorescent	Colorless, Bright Blue Fluorescent	15 min.
28 1-Methoxy-9,10-diphenyl anthracene	Colorless, Not Fluorescent	Colorless, Blue-green Fluorescent	15 min.
29 BPEA	Slightly orange, Weak Fluorescence	Yellow. Colored, Yellow-Green Fluorescent	30 min.
30 Rubrene	Colorless, Weak Fluorescence	Pink colored, Orange Fluorescent	2 min.
31 BPET	Colorless (dilute), Dull gray (concentrated), Weak Fluorescence	Colorless or red Orange Fluorescent	15 min.
32 1,2,8,9-Dibenzpentalene	Colorless, Not Fluorescent	Colorless, Yellow-orange Fluorescent	5 min.

A small amount of this material was dissolved in benzene and the solution allowed to dry on filter paper to leave a colorless and non-fluorescent circle. Information was then recorded by means of a heated (about 200°C.) object placed on the treated paper (about 1 second), when a yellow-green fluorescent image was produced. Longer contact time caused the image to be transferred to the underlying substrate.

The images were bleached by 3,500 Å ultraviolet (10 minutes, Rayonet Photochemical Reactor) and yellowish fluorescent images regenerated by the heated objects.

A higher molecular weight polyethylmethacrylate (PEMA) film containing a small amount of the above dibromo compound was weakly yellow colored and not fluorescent. Irradiation with 2,537 Å ultraviolet light (H100 A4/T Mercury lamp with glass envelope removed) for 1—2 minutes produced yellow colored and greenish fluorescent images in the film. Applying the heated (about 200°C.) objects also produced similar images in this film.

## THERMAL IMAGING OF PLASTIC FILMS CONTAINING AN AROMATIC ENDOPEROXIDE

### Examples 34 to 42

Plastic films were prepared containing DPA.O<sub>2</sub>.

All the films were solvent cast on glass microscope slides (except PVA). Each film of Examples 34 to 39 contained less than 40 mg. DPA.O<sub>2</sub> per gram of polymer. The films of Examples 40 to 42 contained compounds as indicated. The information images were formed by applying a heated (150—200°C.) key to the sample for approximately 1—2 seconds. All the samples became soft and sticky, and some (see Table II) became brown when too hot (>200°C.) an object was used. The bleaching studies were performed in the Rayonet Photochemical Reactor with 3,500 Å ultraviolet lamps.

### Example 34

**PEMA:** High molecular weight polyethyl methacrylate, "Elvacite" (registered Trade Mark) 2042, DuPont Chemical Co. The films were cast from a mixture of toluene, methyl-ethyl-ketone and ethanol. The imaging (by the heated key) and bleaching (by 3,500 Å U.V.) was repeated three times on one area of the film.

### Example 35

**CAB:** Cellulose acetate butyrate, EAB—380—20, Eastman Chemical Co. The films were cast from acetone.

### Example 36

**VAGH:** "Bakelite", (registered Trade Mark) vinyl chloride-acetate copolymer with about 91% vinyl chloride. The films were cast from a mixture of acetone and methyl ethyl ketone.

### Example 37

**PVC:** Polyvinyl chloride. The films were cast from methylene chloride.

### Example 38

**PVA:** Polyvinyl alcohol, "Elvanol" (registered Trade Mark) 71—30, DuPont Chemical Co. The films were cast from a mixture of ethanol and water. An attempt to dry the film under reduced pressure gave large tough bubbles, which were cut into samples for testing.

### Example 39

**H—15 Acrylite:** The films were cast from benzene.

### Example 40

A clear, colorless and weakly fluorescent H—15 Acrylite film (American Cyanamid Co. polymethyl methacrylate) containing 6% by weight of 1-methoxy-9,10-diphenylanthracene endoperoxide gave a colorless but good blue fluorescent material image (and bubbles) when the heated key was applied.

### Example 41

A clear, weakly yellow colored and weakly blue fluorescent PEMA film containing 1% by weight BPET endoperoxide gave an orange-pink colored and orange fluorescent material image (and bubbles), when the heated key was applied. This image was bleached after one day in the laboratory fluorescent lights. The initial endoperoxide

was also prepared by exposing the PEMA—BPET film to the laboratory lights for four days.

#### Example 42

A clear, weakly yellow-colored and weakly blue fluorescent PEMA film containing 1% by weight rubrene endoperoxide gave a pink-colored and yellow-orange fluorescent material image (and bubbles), when the heated key was applied. The image was bleached, and the endoperoxide prepared as described above for the PEMA—BPET film.

The results of thermal imaging are illustrated in Table II for Examples 34 to 39. As may be seen, the system can be reversible or irreversible depending on the plastic matrix.

TABLE II

Plastic Films Containing DPA.O<sub>2</sub>

Polymer	Initial Appearance	Image Developed by Heat	Extent of Bleaching by U.V.
34 PEMA	Clear, colorless, non-fluorescent	Colorless, blue fluorescent (bubbles).	2 hrs.: Completely bleached.
35 CAB	Cloudy-white, non-fluorescent	Clear, colorless, blue fluorescent	2 hrs.: Almost bleached
36 VAGH	Clear, colorless, non-fluorescent.	Colorless, blue fluorescent(*)	2—3 hrs.: Some bleaching.
37 PVC	Foamy, colorless, non-fluorescent	Colorless, blue fluorescent*	2 hrs.: Only slightly bleached
38 PVA	Clear, colorless non-fluorescent.	Cloudy white, blue fluorescent(*)	2 hrs.: No bleaching
39 H-15 Acrylite	Clear, colorless, non-fluorescent	Colorless, blue fluorescent (bubbles)	3 hrs.: No bleaching

(\*) Too much heat caused the polymer to become brown.



# IMAGING BY INFRARED IRRADIATION OF PEMA FILMS CONTAINING DPA.O<sub>2</sub>

## Examples 43 to 48

5 All films were prepared with high molecular weight polyethyl methacrylate (PEMA) of Example 34 and were cast on glass slides from a mixture of acetone, methyl-ethyl-ketone, toluene and ethanol. Charcoal or an infrared absorber is included as a sensitizing agent in some cases. The infrared absorbers ("Cyasorb" IR—117 and "Cyasorb" IR—165) are products of American Cyanamid Company, and "Cyasorb" is a registered Trade Mark. All the tests were performed by holding the sample about 5 inches from a 250W, G. E. infrared bulb. The additives increased the sensitivity of the system to infrared light in the following order: None < IR—117 < IR—165 < charcoal. Lower concentrations of the additives were still effective as sensitizers for this system. 5 10

15 The reversibility study was performed with Example 44. Thus, colorless but good blue fluorescent images were produced by irradiation for 1—2 minutes with the 250W, G. E. infrared light bulb (sample about 3 inches from the bulb). The images were bleached after 15—45 minutes irradiation with 3,500 Å U.V. light (Rayonet Photochemical Reactor). This process of imaging and bleaching was repeated 12 times. After this series, the film was still colorless (except for the black charcoal particles). 15 20

The fact that irradiation from the above infrared light bulb converts the precursor to a fluorescent material indicates that also an infrared input information pattern could be recorded by the method of this invention.

The results are shown in Table III.

TABLE III

— Infrared Irradiation of PEMA Films Containing DPA.O<sub>2</sub>

Example	1/2 Min. Irradiation	1 Min. Irradiation	3 Min. Irradiation
—42	5% DPA.O <sub>2</sub> ; clear, colorless and non-fluorescent.	No image.	Weak blue. Fluorescent image (no visible color).
43	5% DPA.O <sub>2</sub> , 6% DARCO, charcoal; colorless, non-fluorescent translucent	Weak blue fluorescent image (colorless).	Very strong blue fluorescent image (colorless); also bubbled.
44	5% DPA.O <sub>2</sub> , 10% IR—117; clear, dark green, non-fluorescent.	No image.	Weak blue fluorescent and slightly brown colored image.
45	5% DPA.O <sub>2</sub> , 3% IR—117; clear, light green, non-fluorescent.	No image.	Good blue fluorescent and slightly yellow-brown colored image.
46	5% DPA.O <sub>2</sub> , 10% IR—165; clear, dark brown non-fluorescent.	No image.	Blue fluorescent and slightly green-brown colored image.
47	5% DPA.O <sub>2</sub> , 3% IR—165; clear, light brown, non-fluorescent.	Very faint blue fluorescent image.	Blue fluorescent and yellow-green colored image.

An additional PEMA film containing 3% DPA.O<sub>2</sub> was cast from toluene, methyl-ethyl-ketone and ethanol and was clear, colorless and weakly fluorescent. When irradiated by infrared as above at 7 cm. for 2 to 5 minutes, a colorless but blue fluorescent image was produced.

#### IMAGING BY ULTRAVIOLET IRRADIATION OF FILMS CONTAINING DPA.O<sub>2</sub>

Examples 49 to 55

The films were the same ones as used in the thermal imaging in Example 44, 10 containing 20—50 mg. DPA.O<sub>2</sub> per gram of polymer. The results are shown in Table IV. The 2,600 Å and 3,000 Å light referred to in Table IV was obtained from a 450W

Xenon lamp in conjunction with a B & L Monochromator (No. 33-86-07) and water filter. The intensity of the light at 2,600 Å was 0.2 mW/cm<sup>2</sup> and at 3,000 Å it was 1.14 mW/cm<sup>2</sup>. The 2,537 Å light was obtained from a 100W mercury lamp (H100 A4/T) with the glass envelope removed. The 3,500 Å light was obtained with the Rayonet Photochemical Reactor using 3,500 Å bulbs. None of the images had any visible color (just the blue fluorescence).

The fact that irradiating from the above ultraviolet lamp in these and also subsequent examples converts the precursor to a fluorescent material indicates that also an ultraviolet input information pattern could be recorded by the method of this invention.

The images produced in Examples 49 to 55 were bleached by 3,500 Å ultraviolet radiation.

TABLE IV

Ultraviolet Irradiation of Films Containing DPA.O<sub>2</sub>

Example	Polymer and Appearance	Image Developed at 2600 Å	Image Developed at 3000 Å
48	High M.W. polyethylmethacrylate; Elvacite 2042; clear, colorless, and non-fluorescent.	5 min.: Good blue fluorescence. 10 min.: Stronger blue fluorescence.	5 min.: Fairly good blue fluorescence. 10 min.: Good blue fluorescence.
49	Cellulose Acetate Butyrate; EAB 380-20; cloudy-white and non-fluorescent.	5 min.: Faint blue fluorescence. 10 min.: Good blue fluorescence.	5 min.: No image. 10 min.: Faint blue fluorescence.
50	Vinyl chloride-acetate copolymer; (≈91% vinyl chloride); VAGH; clear, colorless, non-fluorescent.	5 min.: Fairly good blue fluorescence. 10 min.: Stronger blue fluorescence.	5 min.: No image. 10 min.: Very faint blue fluorescence. 20 min.: Very faint blue fluorescence.
51	Polyvinyl Chloride; foam-like, colorless, non-fluorescent.	5 min.: Good blue fluorescence. 10 min.: Stronger blue fluorescence.	5 min.: No image. 10 min.: Faint blue fluorescence. 20 min.: Stronger blue fluorescence.
52	H15 Acrylite Molding Compound; clear, colorless, non-fluorescent.	5 min.: Very good blue fluorescence.	5 min.: Weak blue fluorescence. 10 min.: Good blue fluorescence.
53	High M.W. polyethylmethacrylate; Elvacite 2042; clear, colorless, and non-fluorescent.	Image Developed at 2537 Å 1 sec.: Blue fluorescence. 5 sec.: Stronger blue fluorescence.	Bleaching at 3500 Å 15 min.: Completely bleached.
54	H-15 Acrylite Molding Compound; clear, colorless, non-fluorescent.	1 sec.: Blue fluorescence. 5 sec.: Stronger blue fluorescence.	3 hrs.: Not bleached.

## Example 56

A film containing 2.7% by weight of DPA.O<sub>2</sub> in H—15 Acrylite Molding Compound was prepared by allowing a methylene chloride solution to dry on a glass slide. The dried film was clear, colorless and only very weakly blue fluorescent. After irradiating the film for about 1 sec. with 2,537 Å ultraviolet light (same lamp as in Example 53), a colorless but good blue fluorescent image was produced.

## Example 57

A film containing 2.3% by weight of DPA.O<sub>2</sub> in H—15 Acrylite Molding Compound was prepared by allowing an acetone solution to dry on a glass slide. The dried film was clear, colorless and only faintly blue fluorescent. After irradiating the film for about 1 second with 2,537 Å ultraviolet light (same lamp as above) a colorless but good blue fluorescent image was produced. A stronger blue fluorescent (and colorless) image was produced after 5 seconds ultraviolet irradiation at 2,537 Å. The intensity of the blue fluorescent image was reduced after 1/2 hour irradiation at 3,500 Å (Rayonet Photochemical Reactor).

A second exposure to 2,537 Å ultraviolet light for 5 seconds increased the intensity of the blue fluorescence slightly. A blue fluorescent image still remained (only slightly reduced intensity) after 3 hours in 3,500 Å ultraviolet light (Rayonet Photochemical Reactor). A third exposure to 2,537 Å ultraviolet light for 5 seconds only slightly increased the intensity of the image. Again, the blue fluorescent image remained after 2-hour exposure to 3,500 Å ultraviolet light. A fourth exposure to 2,537 Å ultraviolet light for 5 seconds increased the intensity of the image only very slightly. Another 1—1/2 hours of ultraviolet irradiation at 3,500 Å only caused a slight reduction in the intensity of the blue fluorescence of the image. The image was slightly yellow colored after all the above irradiations. Since the image could not be bleached, this is an example of a one-way system.

## Example 58

A film containing 3.4% by weight of DPA.O<sub>2</sub> in H—15 Acrylite Molding Compound was prepared by allowing a benzene solution to dry on a glass slide. The dried film was clear, colorless and only weakly blue fluorescent. After irradiating the film for about 1 second with 2,537 Å ultraviolet light, a colorless but good blue fluorescent image was produced. The Examples 56, 57 and 58 show that the system is not dependent upon the solvent used to cast the film.

## Example 59

A film containing 3% by weight of DPA.O<sub>2</sub> in high molecular weight polyethyl methacrylate (Elvacite 2042) was prepared by allowing a benzene-toluene-methyl ethyl ketone solution to dry on a glass slide. The dried film was clear, colorless, and only faintly blue fluorescent. After irradiating the film for about 1 second with 2,537 Å light, a colorless but very good blue fluorescent image was produced. Another colorless but good fluorescent image was produced by irradiating the film for 5 sec. with 2,537 Å ultraviolet light. This image was completely bleached after 15 minutes irradiation with 3,500 Å ultraviolet light (Rayonet Photochemical Reactor). This process of imaging and bleaching was repeated 21 times on the same area of the film. The resulting film was still colorless. This is an example of the reversible formation of colorless but blue fluorescent images by ultraviolet light.

## Example 60

A film containing 6% by weight of 1-methoxy-9,10-diphenylanthracene endoperoxide in H—15 Acrylite Molding Compound was prepared by allowing a benzene solution to dry on a glass slide. The dried film was clear, colorless and faintly blue fluorescent. After irradiating the film for about 1 second with 2,537 Å ultraviolet light, a colorless but good blue fluorescent image was produced.

## Example 61

A film containing 10% by weight of DPA.O<sub>2</sub> in high molecular weight polyethyl methacrylate was prepared as described in Example 39 with the exception that this film was cast on 3 mil bond-coated "Mylar" (registered Trade Mark). The dried film was clear, colorless, weakly blue fluorescent, and 1.5 mils thick. Five different colorless but blue fluorescent images were produced on this film by irradiation with 2,537 Å ultraviolet light for different lengths of time.

Image No. 1: 1—2 seconds of exposure gave colorless and weakly blue fluorescent image.

Image No. 2: 5 seconds of exposure gave colorless and stronger blue fluorescent image.

Image No. 3: 20 seconds of exposure gave colorless and still stronger blue fluorescent image.

5 Image No. 4: 40 seconds of exposure gave colorless and only slightly stronger blue fluorescent image. 5

Image No. 5: 1 minute of exposure gave colorless and blue fluorescent image of same intensity as in No. 4.

10 Image No. 5 was completely bleached after 10 minutes of irradiation with 3,500 Å ultraviolet light. This image No. 5 (as well as all the other [Nos. 1—4] remained colorless after the above irradiations. 10

#### Example 62

15 A benzene solution of  $\text{DPA}\cdot\text{O}_2$  was allowed to dry on paper to leave a colorless, non-fluorescent circle containing approximately 0.1 mg.  $\text{DPA}\cdot\text{O}_2$  per  $\text{cm}^2$ . Irradiating the paper for 1—2 seconds with the 2,537 Å U.V. light at a distance of 5 inches (of Example 53) gave a blue fluorescent and slightly yellow-colored image. The image was completely bleached after 15 minutes exposure to 3,500 Å U.V. light (Rayonet), and the cycle repeated four times. 15

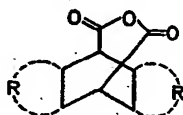
#### WHAT WE CLAIM IS:—

20 1. A method of recording information on a substrate, which comprises the steps of (a) providing a substrate which carries a fluorescer precursor substance which is at least substantially non-fluorescent (as herein defined) but which is capable of being converted to a chemically different fluorescent substance on being heated or on the application of ultraviolet light, and (b) heating said substrate or applying ultraviolet light thereto, in a pattern corresponding to the information to be recorded thereon, said heating or applied ultraviolet light being such as to effect conversion of said fluorescer precursor substance to a fluorescent substance capable of fluorescing under ultraviolet or visible light whereby the information is recorded on said substrate as a pattern of fluorescent substance which corresponds to the applied information pattern. 20

25 2. A method according to Claim 1, wherein said substrate is heated by means of infra-red radiant energy. 25

30 3. A method according to Claim 1, wherein said fluorescer precursor substance is a 2-(2-furyl)-3-acylchromone or a 2-(2-thienyl)-3-acylchromone. 30

35 4. A method according to Claim 1 or Claim 2, wherein said fluorescer precursor substance is an aromatic anhydride compound of the formula: 35



wherein  represents an aromatic residue.

40 5. A method according to Claim 4, wherein said fluorescer precursor substance is 9,10-diphenyl-9,10-dihydroanthracene-9,10-anhydride, or 9,10-diphenyl-1,4-dihydroanthracene-1,4-anhydride. 40

6. A method according to Claim 1 or Claim 2, wherein said fluorescer precursor substance is an aromatic endoperoxide.

45 7. A method according to any preceding claim, wherein said substrate is paper or a plastics material, and wherein said fluorescer precursor substance is incorporated into a coated onto said substrate. 45

8. A method of recording information on a substrate, according to Claim 1 and substantially as hereinbefore described.

9. A substrate on which has been recorded information by a method according to any preceding claim.

50 10. A substrate on which has been recorded information by a method according to Claim 3. 50

11. A substrate on which has been recorded information by a method according to Claim 4.

55 12. A substrate on which has been recorded information by a method according to Claim 6. 55

13. A method of retrieving information from a substrate according to any one of Claims 9—12, which method comprises applying to said substrate U.V. or visible light of a wavelength such as to cause said fluorescent substance to fluoresce.

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